Effects of Surface Oxide Layer and Metalloid Elements on the Hydrogen Absorption and Desorption Characteristics of Amorphous Ti-Ni and Zr-Ni Alloys

Effects of Surface Oxide Layer and Metalloid Elements on the Hydrogen Absorption and Desorption Characteristics of Amorphous Ti-Ni and Zr-Ni Alloys*

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Synopsis

Effects of surface oxide layer and metalloid elements on the hydrogen absorption and desorption characteristics of amorphous $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ alloys were investigated by a volumetric method and AES. Both hydrogen absorption characteristics and surface condition of amorphous alloys depended sensitively on the atmosphere exposed during rapid quenching. The amorphous $Ti_{67}Ni_{33}$ alloy prepared in air hardly absorbed hydrogen due to the formation of a thick oxide layer on the surface. This result suggested that one should take the effect of the atmosphere into account for understanding the hydrogen absorption and desorption characteristics of amorphous alloys. Furthermore, it became clear that the addition of metalloid elements to the metal- metal type amorphous alloys was deleterious for hydrogen absorption, because small holes in the amorphous structure which were to be preferential sites of hydrogen atoms were probably occupied by metalloid elements.

I Introduction

It is expected that the metal-metal type amorphous alloys consisting of an early transition metal (Ti,Zr,Hf, etc) and a late transition metal (Mn,Fe,Co,Ni, etc) might absorb a large quantity of hydrogen because of a high absorbing ability of early transition metals and a large number of small holes in amorphous structure, which are considered to be preferential sites of hydrogen atoms. From this point of view, it has recently been tried to investigate the hydrogen absorption

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properties of some amorphous alloys such as Cu-Ti[1)2)], Zr-Ni[3)] and Zr-(Fe,Co,or Ni)[4)] and found that these alloys can absorb fairly large quantity of hydrogen even in the amorphous state.

It has generally been known that the absorption of hydrogen is very sensitive to the surface condition of alloys. Therefore, the absorbing characteristics of amorphous alloys seem to be influenced by the atmosphere exposed during rapid quenching. It is also considered that the hydrogen absorption of amorphous alloys might be influenced by the addition of metalloid elements having small atomic sizes. Because the atoms of metalloids occupy small holes in the amorphous structure which are considered to be preferential sites of hydrogen atoms. In the present work, therefore, the effects of the surface condition and the addition of metalloid elements on hydrogen absorption and desorption were examined using two amorphous alloys of $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$.

II Experimental

$Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ binary and $(Ti_{67}Ni_{33})_{0.9}\cdot A_{0.1}$ (A= B or Si) ternary alloys were arc melted from highly pure elements under an argon atmosphere. The buttons were repeatedly turned over and remelted to ensure homogeneity of compositions.

Continuous ribbon specimens of about 1mm width and 0.01mm thickness were prepared using a conventional melt spinning technique. The as-quenched structure was identified by X-ray diffraction and transmission electron microscopy. The crystallization temperature (Tx) was determined in argon by a differential thermal analyzer (DTA) at a heating rate of about 8.33×10^{-2}/s.

The absorption or desorption of hydrogen was examined by using an apparatus illustrated schematically in Fig.1.This apparatus consists of stainless steel tubes, high pressure valves, connectors, a pressure transducer, a reservoir, a vacuum pump, a high pressure hydrogen gas cylinder, a reactor and a volumetric buret. The reactor can be heated by an electric furnace controlled within $\pm$ 1K.

All samples were first degassed for 7.2Ks at 473K in a reduced atmosphere of about 2×10^{-1}Pa. After degassing,they were heated for 18Ks at 473K in highly pure hydrogen gas (99.99999%) of 5MPa.
The amount of absorbed hydrogen in the samples was estimated from the pressure change in the reactor. The amount of desorbed hydrogen was measured by heating the hydrogen-absorbed sample and by collecting the released hydrogen into an inverted volumetric buret.

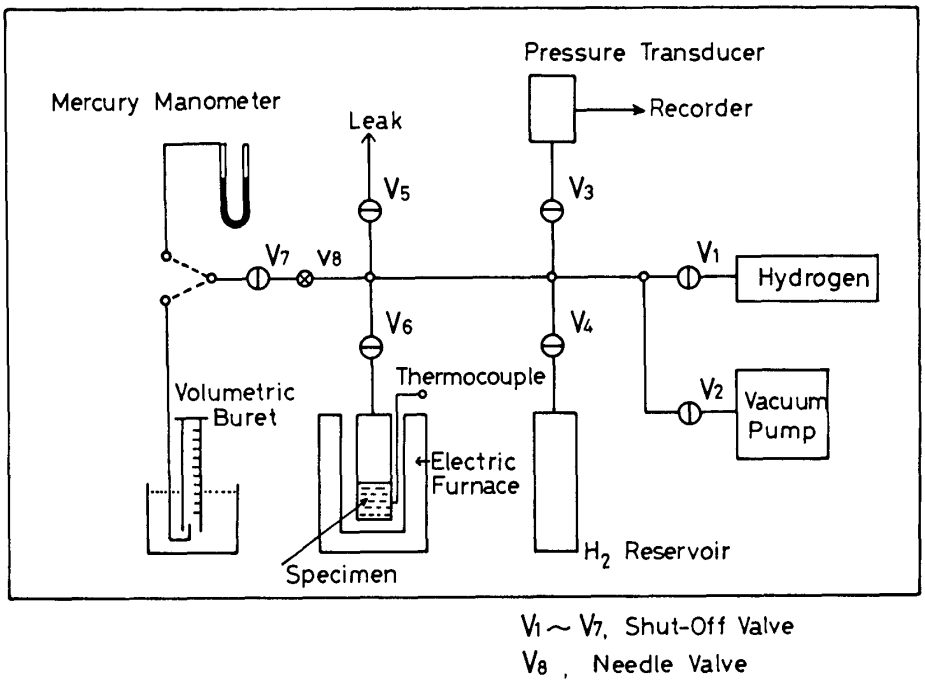

Fig.1 A schematic diagram of an apparatus for measuring the amounts of absorption and desorption of hydrogen.

III Results

Prior to the experiments on the absorption and desorption of hydrogen, it was confirmed by X-ray diffraction and electron microscopy that the structure of as- prepared samples was of an amorphous single phase. As an examle, Photo.1 shows the electron micrograph and diffraction pattern of the as-prepared $Zr_{50}Ni_{50}$ amorphous alloy. Lack of contrasts in the bright field image and a feature of diffused haloes on the diffraction pattern clearly indicate that the rapid quenched alloy has an amorphous structure. In addition, the data of DTA were taken with as-prepared and subsequently hydrogen- absorbed samples. Fig.2 is the DTA data of the $Ti_{67}Ni_{33}$ amorphous alloy as an example. In the figure it is observed that a well defined exothermic peak appears at 778 K as is similar for other amorphous alloys and there is no change in the crystallization temperature Tx by hydrogen absorption.

1. Effect of surface condition of sample

Both amorphous alloys of $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ hardly absorbed hydrogen near room temperature. With heating the sample, however, the absorption of hydrogen started and increased slowly. In the present

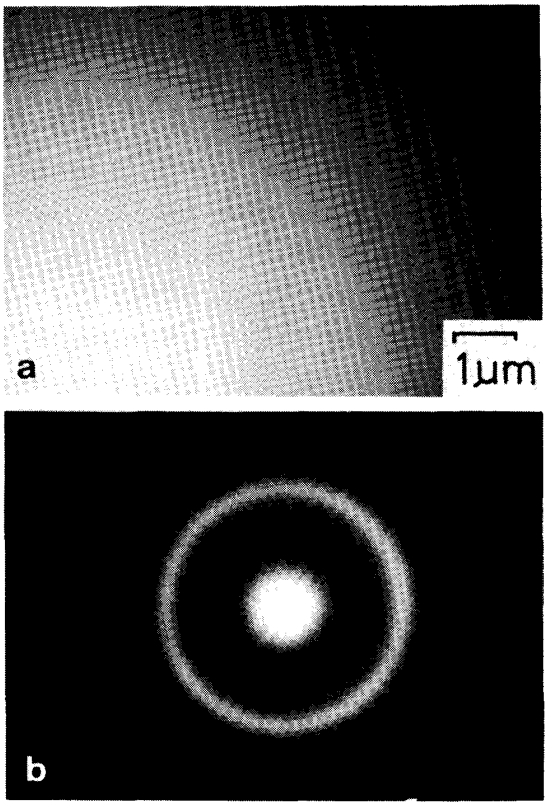

Photo. 1 A bright field micrograph and the corresponding diffraction pattern for the rapid quenched $Zr_{50}Ni_{50}$ alloy.

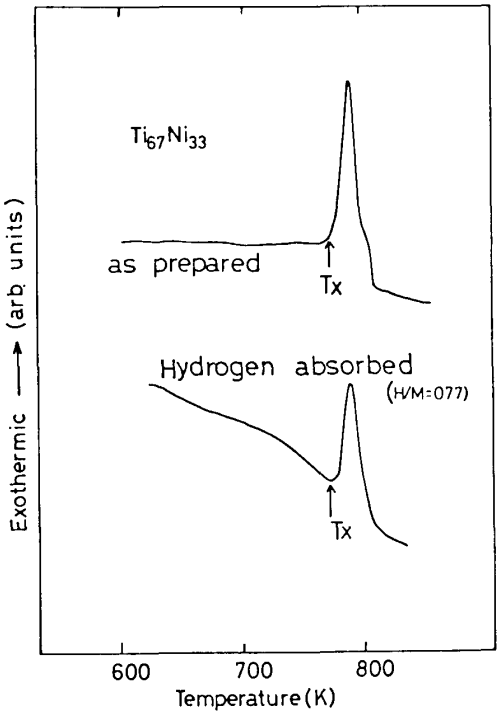

Fig. 2 DTA curves for both as-quenched and hydrogen charged $Ti_{67}Ni_{33}$ amorphous alloys.

Table 1 The amount of absorbed hydrogen for $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ amorphous alloys quenched in air or argon.

Alloy	Condition	Absorbed amount of hydrogen (H/M)
$Ti_{67}Ni_{33}$	Quenched in air Quenched in Ar	negligible small ~0.8
$Zr_{50}Ni_{50}$	Quenched in air Quenched in Ar	~0.8 ~0.9

work, all samples were hydrogenated for 18 Ks at 473 K, which is the heating condition enough to prevent the crystallization of samples. In Table 1, the amount of hydrogen absorbed in the sample by hydrogenation is shown with both amorphous alloys of $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$. In the table, the effect of atmosphere exposed during rapid quenching is also seen. The amount of absorbed hydrogen is of the order of about 0.8-0.9 H/M for both alloys prepared in argon. In the case of the samples prepared in air, however, there is a distinct difference in the value;that is, the $Ti_{67}Ni_{33}$ alloy hardly absorbs hydrogen, while the $Zr_{50}Ni_{50}$ alloy absorbs almost the same order to the alloy prepared in argon.

Fig. 3 represents the absorbed hydrogen-time curves during heating at 473 K under a hydrogen pressure of 5 MPa for the $Ti_{67}Ni_{33}$ amorphous alloys prepared under various conditions. In the figure, the curve shown by a dotted line is the result on the sample which is kept always in argon atmosphere in the whole process before hydrogenation. The absorbed amount of the sample quenched in air is negligible small even after heating for 50 Ks. On the other hand, the sample quenched in argon absorbs swiftly with holding time and the absorbed value reaches about 0.8 H/M. The absorbing ability of hydrogen further increases in the case of the sample unexposed to air during preparation as shown by dotted line.

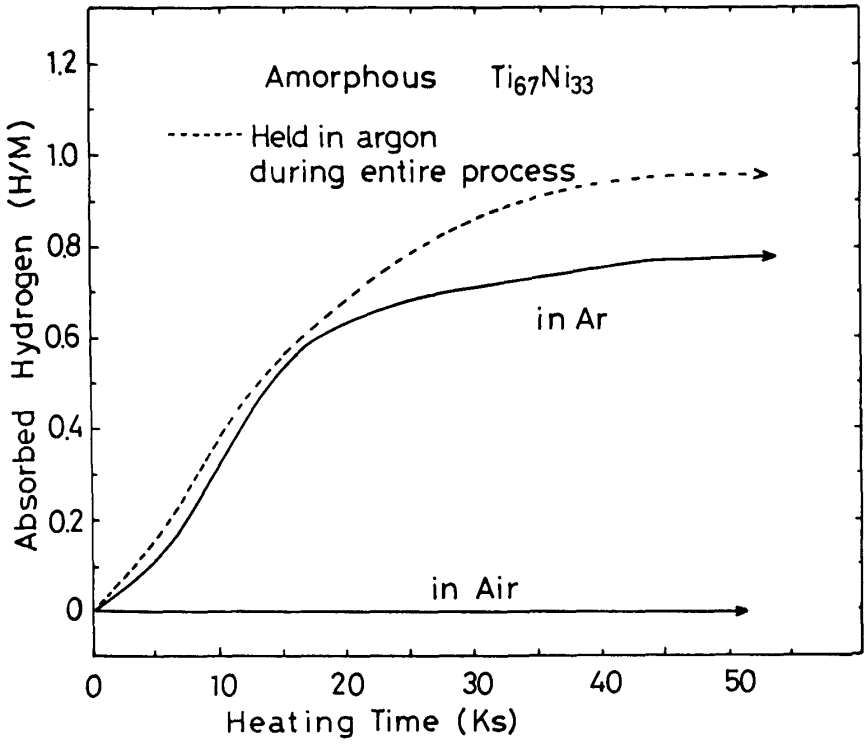

Fig.3 The absorbed hydrogen-time curves during heating at 473 K for the $Ti_{67}Ni_{33}$ amorphous alloys.

In Figs. 4 and 5, it can be seen again that the desorbed value depends on the atmosphere exposed during rapid quenching. Figures 4 and 5 illustrate the amount of desorbed hydrogen by heating after hydrogenation for $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ amorphous alloys, respectively. In these figures, it can be seen again that the desorbed value depends on the atmosphere exposed during rapid quenching. In particular, a remarkable differnce between the samples quenched in air and argon is observed for $Ti_{67}Ni_{33}$ alloy.

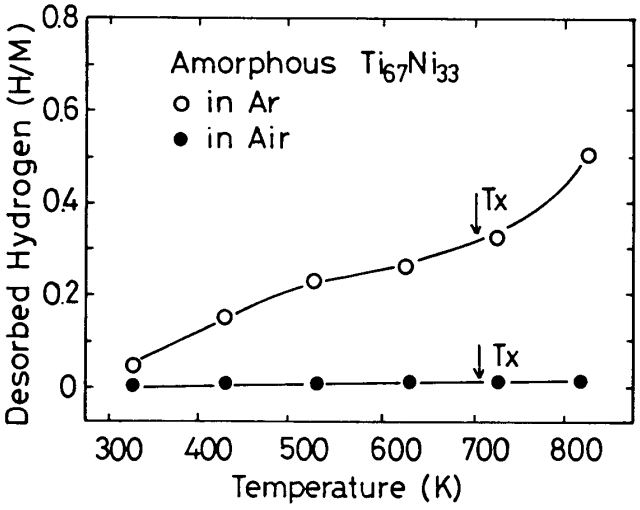

Fig. 4 The desorbed amount of hydrogen as a function of heating temperature for $Ti_{67}Ni_{33}$ amorphous alloys quenched in air or argon.

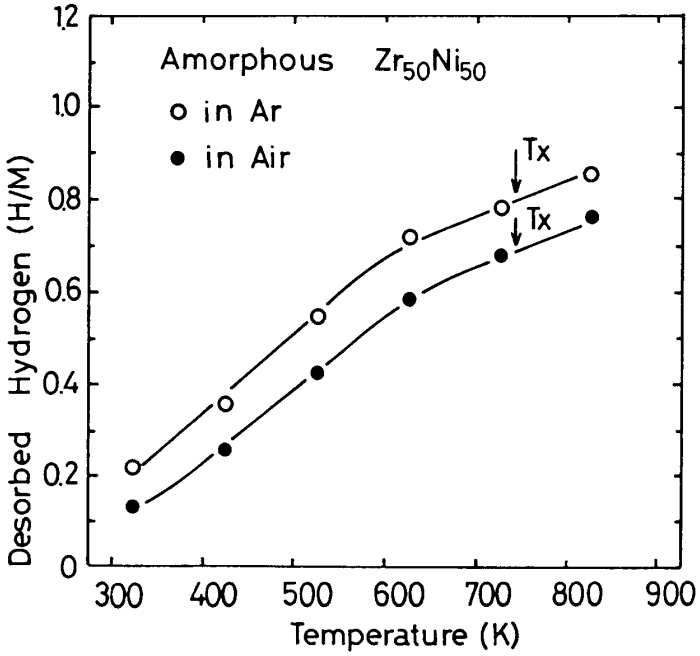

Fig. 5 The desorbed amount of hydrogen as a function of heating temperature for $Zr_{50}Ni_{50}$ amorphous alloys quenched in air or argon.

Judging from these data, the absorption and desorption properties of hydrogenated amorphous alloys are very sensitive to the alloy composition and the surface condition. In order to clarify reason why there is a distinct difference in the ability of absorption and desorption depending on the alloy composition, the depth profiles of components in the surface layer were examined by using AES. As representative data, Fig. 6 shows a AES spectrum for the $Ti_{67}Ni_{33}$ amorphous alloy quenched in air, wherein the existence of oxygen in surface layer is clearly seen besides constituents in the alloy.

The depth profiles of these elements are shown in Figs. 7 and 8. With sputtering time, the concentration of oxygen decreases sharply,

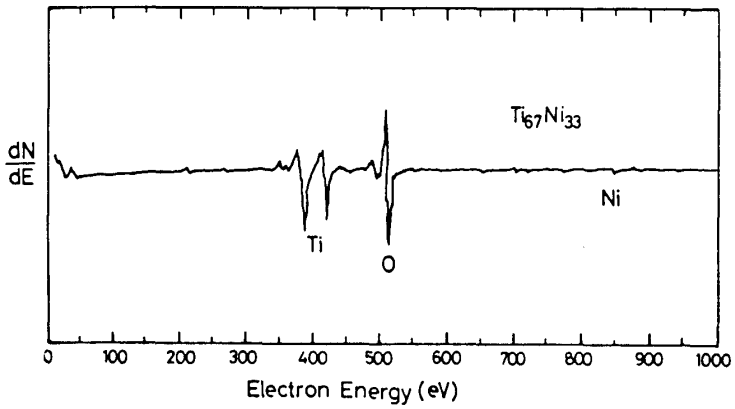

Fig.6 A typical AES spectrum for the $Ti_{67}Ni_{33}$ amorphous alloy quenched in air.

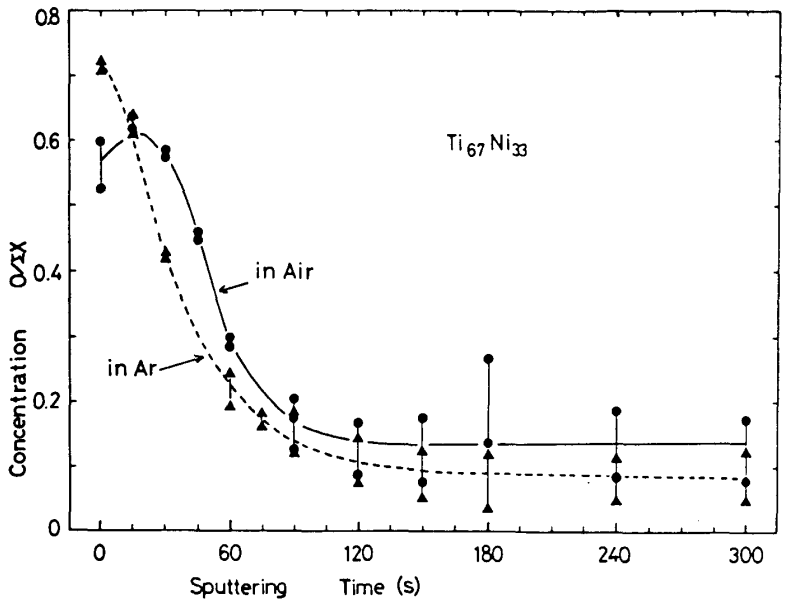

Fig.7 Depth profiles of oxygen for $Ti_{67}Ni_{33}$ amorphous alloys.

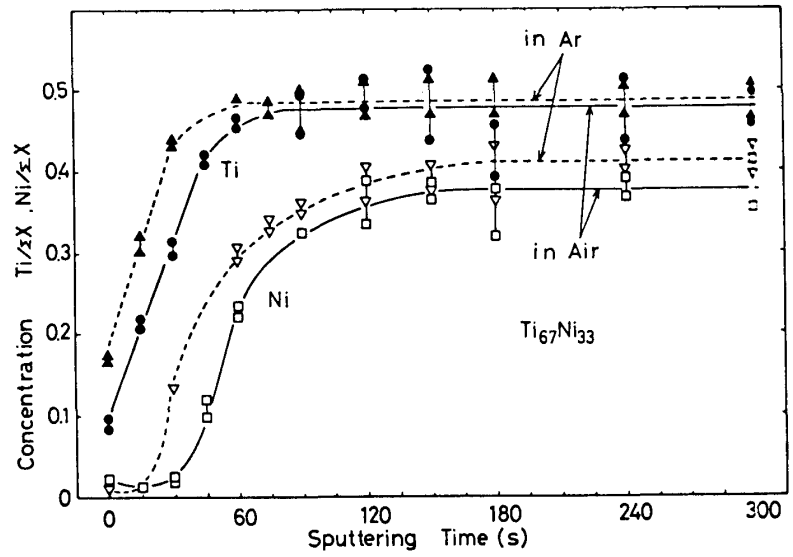

Fig. 8 Depth profiles of titanium and nickel for the $Ti_{67}Ni_{33}$ amorphous alloys.

while the nickel and titanium concentration increase, and after sputtering for 60-120s the concentration of each element reaches the level of the bulk concentrations. In these figures, it should be noticed that the oxygen-rich layer near the surface of the sample quenched in air is thicker than that of the sample quenched in argon. In contrast to this alloy, the thickness of the oxygen- rich layer for the $Zr_{50}Ni_{50}$ amorphous alloy is almost same in both cases of in air and in argon as seen in Figs. 9 and 10. Therefore, a remarkable lowering of hydrogen absorption and desorption of $Ti_{67}Ni_{33}$ amorphous alloys quenched in air appears to be due to a thick oxide layer on the surface of sample formed during rapid quenching. These results indicate that one should take the surface condition into account for understanding the hydrogen absorption and desorption characteristics of amorphous alloys.

It has been known well that the hydrogen- absorption behaviors of various metals, alloys and intermetallic compounds which form metal-hydrides by exothermic reactions are remarkably sensitive to the chemical composition and the condition of surface[5], because molecular hydrogen has to be dissociated on the surface of materials in absorption process and in desorption process hydrogen atoms in materials recombine to hydrogen molecule . In particular, surface oxide layer is considered to impede the hydrogen absorption.

The oxide layer is usually removed mechanically or by heating the material in vacuum or hydrogen atmosphere. Such heat treatments are known as " activation treatment". In the case of amorphous alloys, however, there is a difficulty that the activation treatment must be performed

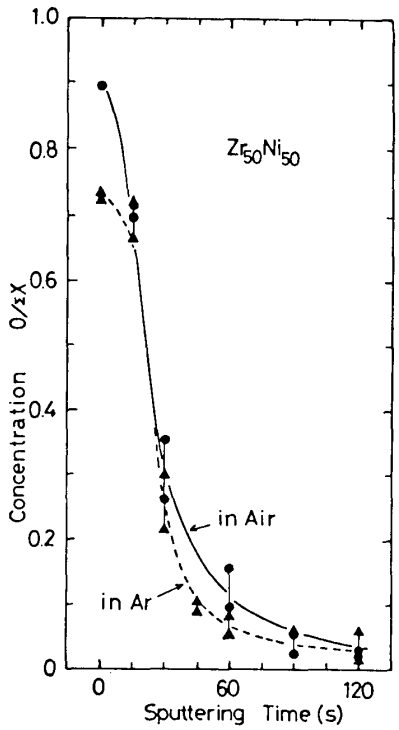

Fig.9 Depth profiles of oxygen for $Zr_{50}Ni_{50}$ amorphous alloys quenched in air or argon.

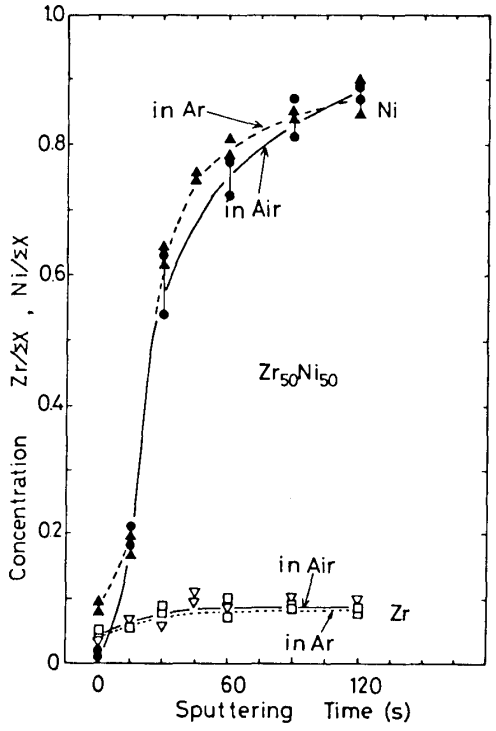

Fig. 10 Depth profiles of zirconium and nickel for $Zr_{50}Ni_{50}$ amorphous alloys quenched in air or argon.

at temperatures lower than their crystallization temperature. Therefore, careful attentions are necessary during preparing the sample of amorphous alloys.

2. Effect of metalloid elements

It is known that the addition of metalloid elements yields a remarkable enhancement of an amorphous forming ability. In the present work, the effect of boron and silicon on the absorption and desorption characteristics of hydrogen was investigated. Figure 11 shows the hydrogen desorption curves of amorphous (solid lines) and crystalline (dotted lines) $Ti_{67}Ni_{33}$ alloys. All amorphous samples were prepared in argon atmosphere in order to prevent the oxidation of samples. The desorption of crystalline alloys is not affected very much by addition of boron and silicon. On the contrary, the value in amorphous state is influenced considerably and decreases by addition of boron and silicon. Especially, a remarkable decrease is induced by addition of boron with a small atomic diameter. Although the reason for such a effect of metalloid elements is uncertain at present, it may be explained by the following inference. That is, the small holes in the

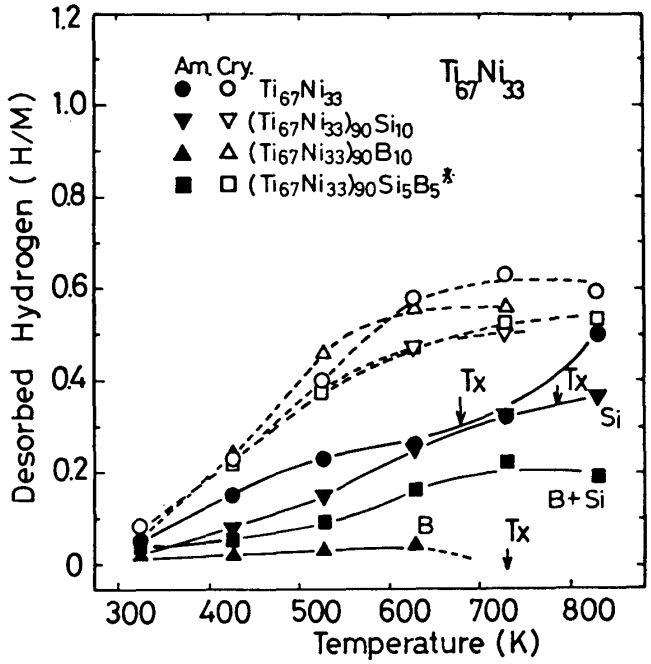

Fig. 11 Effects of boron and silicon on the desorption properties for both amorphous and crystalline $Ti_{67}Ni_{33}$ Alloys .

amorphous structure which are considered to be preferential sites of hydrogen atoms are occupied by these metalloid atoms. Thus, it may be stated that the dissolution of metalloid elements is deleterious for hydrogen storage nature of the metal-metal type amorphous alloys.

IV Summary

Effects of the surface oxide layer and the metalloid addition on the hydrogen absorption and desorption characteristics of the amorphous $Ti_{67}Ni_{33}$ and $Zr_{50}Ni_{50}$ alloys were investigated by a conventional volumetric method and AES. It was found that both characteristics of hydrogen - absorption and desorption of these amorphous alloys were very sensitive to the atmosphere exposed during rapid quenching. In particular, the $Ti_{67}Ni_{33}$ amorphous alloy quenched in air did not absorb hydrogen due to a thick surface oxide layer. On the other hand, the $Zr_{50}Ni_{50}$ amorphous alloy could be hydrogenated in spite of the preparation in air, but the desorbed amount of hydrogen was slightly less than that quenched in argon. Therefore, it was pointed out that the atmosphere exposed during quenching should be taken into account for understanding the hydrogen absorption and desorption characteristics of amorphous alloys.

Effect of addition of boron and silicon to $Ti_{67}Ni_{33}$ amorphous alloy was examined. As a result, it was found that those additions were very deleterious for hydrogen storage of the metal-metal type amorphous alloys, because the small holes in the amorphous structure which were considered to be the preferential sites of hydrogen atoms were probably occupied by metalloid atoms.

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